PATENT COOPERATION TREATY

RECEIVED
JAN 30 2001
PATENT RECORDS CENTER

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

MAGEE, Thomas H.
E.I. DU PONT DE NEMOURS AND COMPANY
Legal/Patent Records Center
1007 Market Street
Wilmington, Delaware 19898
ETATS-UNIS D'AMERIQUE

JMS

PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY EXAMINATION REPORT
(PCT Rule 71.1)

Date of mailing *(day/month/year)*	19.01.2001
Applicant's or agent's file reference PE0612 PCT	**IMPORTANT NOTIFICATION**

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US99/25106	26/10/1999	27/10/1998

Applicant
E.I. DU PONT DE NEMOURS AND COMPANY et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.

2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.

3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. **REMINDER**

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Exhibit

REY NOTED

Name and mailing address of the IPEA/	Authorized officer
European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Schuster-Kaechele, W Tel.+49 89 2399-2281

Form PCT/IPEA/416 (July 1992)

27 APR 2001

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
PE0612 PCT		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US99/25106	26/10/1999	27/10/1998
International Patent Classification (IPC) or national classification and IPC G03F7		
Applicant E.I. DU PONT DE NEMOURS AND COMPANY et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 5 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 8 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☒ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
28/04/2000	19.01.2001
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Randez Garcia, F Telephone No. +49 89 2399 2234

Form PCT/IPEA/409 (cover sheet) (January 1994)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/US99/25106

I. Basis of the report

1. This report has been drawn on the basis of *(substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).)*:
Description, pages:

1,4-19,21-66	as originally filed			
2,2a,3,3a,20	as received on	01/12/2000	with letter of	01/12/2000

Claims, No.:

18 (part),19-22	as originally filed			
1-17,18 (part), 23-29	as received on	01/12/2000	with letter of	01/12/2000

Drawings, sheets:

1/1	as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

   These elements were available or furnished to this Authority in the following language: , which is:

   - ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
   - ☐ the language of publication of the international application (under Rule 48.3(b)).
   - ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

   - ☐ contained in the international application in written form.
   - ☐ filed together with the international application in computer readable form.
   - ☐ furnished subsequently to this Authority in written form.
   - ☐ furnished subsequently to this Authority in computer readable form.
   - ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
   - ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

   ☐ the description, pages:
   ☐ the claims, Nos.:
   ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

   (Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-29
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-29
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-29
	No:	Claims	

2. Citations and explanations
   see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

Re Item V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1). The closest prior art is represented by the following documents:

D1: YAMANA M ; ITANI T ; YOSHINO H ; HASHIMOTO S ; TANABE H ; KASAMA K: 'Deblocking reaction of chemically amplified ArF positive' PROC. SPIE - INT. SOC. OPT. ENG., vol. 3333, no. 1, June 1998 (1998-06), pages 32-42, XP002130419 Washington, USA

D2: EP-A-0 473 547 (CIBA-GEIGY AG) 4 March 1992 (1992-03-04)

2). D1 discloses chemically amplified, ArF, positive-working photoresists. Among the resists described therein (see fig. 1, particularly compound a), poly(carboxytetracyclododecyl methacrylate$_{70}$-co-tetrahydropyranylcarboxytetracyclododecyl methacrylate$_{30}$) meets all the requirements stated in present claim 1, except that the branch segments are not polymeric and have a number average molecular weight of less than 1000. Therefore, claim 1 is not anticipated by the disclosure of D1. Since process claim 27 is also characterised by this limiting feature, its subject-matter is also novel with regard to D1.

3). D2 discloses certain olefinically unsaturated onium salts which can be polymerised and used as photosensitive copolymers in photoresist compositions (see abstract). The photosensitive copolymers represented in claim 6 of D2 by formula (VII) are branch copolymers containing protected acid groups and acid-generating groups. However, they do not meet the requirements specified in present claims 1 and 27 because the branch segments are not polymeric and have a number average molecular weight of less than 1000. Hence, the subject-matter of claims 1 and 27 is not anticipated by D2.

4). Furthermore, none of D1 and D2 suggests that the pendent moieties containing protected groups should have molecular weights of at least 1000 in order to attain good plasma etch resistance and adhesive properties. Consequently, the subject-matter of claims 1 and 27 involves an inventive step over the prior art considered (Article 33(2) and (3) PCT).

5). Claims 2-26 and 28-29 are dependent on claims 1 and 27, respectively. They concern particular embodiments of the new and inventive subject-matter contained in claims 1 and 27 and meet, therefore, the requirements of Article 33(2) and (3) PCT.

Re Item VIII

Certain observations on the international application

6). The description is not in conformity with the claims as required by Rule 5.1(a)(iii) PCT. In particular, some statements on page 4, lines 13 and 19, and page 5, line 15, are not in agreement with the limitation included in claims 1 and 27 concerning a number average molecular weight of at least 1000.

(obtained using an F_2 laser source) may be used for future microelectronics fabrication using 0.100 μm or less design rules. The opacity of traditional UV and deep-UV organic photoresists at 193 nm precludes their use in single-layer schemes at this wavelength. Recently new photoresist compositions comprising cycloolefin-maleic anhydride alternating copolymers have been shown to be useful for imaging of semiconductors at 193 nm (see F. M. Houlihan et al., Macromolecules, 30, pages 6517-6534 (1997); T. Wallow et al., SPIE, Vol. 2724, pages 355-364; and F. M. Houlihan et al., Journal of Photopolymer Science and Technology, 10, No. 3, pages 511-520 (1997)).

Comb polymers are a particular class of branched polymers wherein one or more branch (polymer) segments are linked along a linear (polymer) backbone segment. Comb polymers may also be described as linear polymers with polymeric arms Such polymers typically are prepared by copolymerizing a conventional monomer with a macromer. Macromers are defined by Kawakami in the "Encyclopedia Of Polymer Science And Engineering", Vol. 9, pp. 195-204 (John Wiley & Sons, New York, 1987) to be polymers of molecular weight ranging from several hundred to tens of thousands, with a functional group at the end that can further polymerize, such as an ethylenic, an epoxy, a dicarboxylic acid, a diol or a diamino group. U.S. Patent 5,061,602 discloses the use of such a polymer as a binding agent in a negative-working photopolymerizable material suitable for producing printing forms or resist patterns. The polymer binder disclosed consists of a film-forming copolymer that has a multi-phase morphology where at least one phase has a glass transition temperature below room temperature and at least one other phase has a glass transition temperature above room temperature. The copolymer has an average molecular weight (weight average) of more than 10,000, and is produced using an ethylenically unsaturated macromer with an average molecular weight (weight average) of 1000 to 100,000. The use of graft (comb) copolymers having acid functionality in certain negative-working photosensitive compositions, such as solder masks, has published (see PCT International Publication No. WO92/15628.

M. Yamana et al., Deblocking Reaction of Chemically Amplified ArF Positive Resists, PROC. SPIE - INT. SOC. OPT. ENG., Vol. 3333, No. 1, pages 32-42 (June 1998) discloses deblocking reaction mechanisms and lithographic performance in chemically amplified positive ArF resists consisting of triphenylsulfonium triflate as an acid generator and the copolymer poly(carboxy-tetracyclododecyl methacrylate$_{70}$-*co*-tetrahydropyranylcarboxy-tetracyclododecyl methacrylate$_{30}$). EP 0 473 547 A (CIBA-GEIGY AG 4 March 1992) discloses certain olefinically unsaturated onium salts which can be polymerized and used as

photosensitive copolymers in photoresist compositions. The photosensitive copolymers disclosed include branch copolymers containing protected acid groups and acid-generating groups.

There is a critical need though for other novel resist compositions for use at 193 nm or lower, and particularly at 157 nm, that have not only high transparency at these short wavelengths but also other suitable key properties, including good plasma etch resistance and adhesive properties. This invention addresses this critical need by providing new advantageous compositions and associated processes, comprising graft (comb) copolymers, which have these key properties.

SUMMARY OF THE INVENTION

The present invention comprises:

(A) a branched polymer containing protected acid groups, said polymer comprising one or more branch segment(s) chemically linked along a linear backbone segment, wherein the branch segment(s) contain at least two repeating monomer units and have a number average molecular weight (M_n) of least 1000.

(B) at least one photoacid generator.

In another embodiment, the invention is a positive photoresist as described supra wherein the photoacid generator is covalently bonded to the branched polymer.

The invention also includes a process for preparing a photoresist image on a substrate comprising, in order:

(W) applying a photoresist composition on a substrate, wherein the photoresist composition comprises:

(a) a branched polymer containing protected acid groups, said polymer comprising one or more branch segment(s) chemically linked along a linear backbone segment, wherein the branched polymer contains sufficient functionality to render the photoresist developable to afford a relief image, upon imagewise exposure to violet or ultraviolet radiation and subsequent heating, and wherein the branch segment(s) contain at least two repeating monomer units and have a number average molecular weight (M_n) of at least 1000;

(b) at least one photoacid generator; and

(c) a solvent;

(X) drying the coated photoresist composition to remove solvent and thereby to form a photoresist layer on the substrate;

(Y) imagewise exposing the photoresist layer to form imaged and non-imaged areas; and

(Z) developing the exposed photoresist layer having imaged and non-imaged areas to form the relief image on the substrate.

The photoresist compositions of this invention have a particularly good balance of desirable properties, including high transparency to near, far, and extreme ultraviolet light, high plasma etch resistance, and projected high resolution characteristics suitable for microelectronic device fabrication.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a plot of absorbance (μm^{-1}) versus wavelength (nm) in the UV region for corresponding random, block, and graft copolymers having the same or similar comonomer compositions.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

Each photosensitive composition of this invention contains a branched polymer, also known as a comb polymer, which contains protected acid groups. The branched polymer has branch segments, known as polymer arms, of limited molecular weight and limited weight ratio relative to a linear backbone segment.

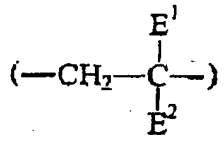
Process Steps

Imagewise Exposure

The photoresist compositions of this invention are sensitive in the ultraviolet region of the electromagnetic spectrum and especially to those wavelengths ≤367 nm. Imagewise exposure of the resist compositions of this invention can be done at many different UV wavelengths including, but not limited to, 365 nm, 248 nm, 193 nm, 157 nm, and lower wavelengths. Imagewise exposure is preferable done with ultraviolet light of 248 nm, 193 nm, 157 nm, or lower wavelenths; is more preferable done with ultraviolet light of 193 nm, 157 nm, or lower wavelengths; and is still more preferably done with ultraviolet light of 157 nm or lower wavelengths. Imagewise exposure can either be done digitally with a laser or equivalent device or non-digitally with use of a photomask. Suitable laser devices for digital imaging of the compositions of this invention include, but are not limited to, an argon-fluorine excimer laser with UV output at 193 nm, a krypton-fluorine excimer laser with UV output at 248 nm, and a fluorine (F2) laser with output at 157 nm. Since, as discussed supra, use of UV light of lower wavelength for imagewise exposure corresponds to higher resolution (lower resolution limit), the use of a lower wavelength (e.g., 193 nm or 157 nm or lower) is generally preferred over use of a higher wavelength (e.g., 248 nm or higher). Specifically, imaging at 157 nm is preferred over imageing at 193 nm for this reason.

Development

The graft copolymers in the photoresists of this invention must contain sufficient functionality for development following imagewise exposure to UV light. Preferably, the functionality is acid or protected acid such that aqueous development is possible using a basic developer such as sodium hydroxide solution, potassium hydroxide solution, or ammonium hydroxide solution. Some preferred graft copolymers in the resist compositions of this invention are protected acid-containing copolymers comprised of at least one acid-containing monomer of structural unit:



in which E^1 is H or C_1-C_{12} alkyl; E^2 is CO_2, E^3 is SO_3E, or other acidic functional group; and E and E^3 are H or C_1-C_{12} alkyl, which is unsubstituted or hydroxyl-substituted. Alkyl groups can contain one to twelve carbon atoms and preferably

What is claimed is:

1. A positive-working photoresist comprising:

(A) a branched polymer containing protected acid groups, said polymer comprising one or more branch segment(s) chemically linked along a linear backbone segment, wherein the branch segment(s) contain at least two repeating monomer units and have a number average molecular weight (M_n) of at least 1000; and

(B) at least one photoacid generator.

2. The photoresist of Claim 1 wherein one of the segments contains greater than 50% of the protected acid groups present in the branched polymer.

3. The photoresist of Claim 2 wherein the branch segment(s) contains greater than 50% of the protected acid groups present in the branched polymer.

4. The photoresist of Claim 1 wherein the branched polymer contains functional groups that are compatible with the photoacid generator, said functional groups being distributed in the branched polymer such that 25 to 100% of the functional groups are present in the segment of the branched polymer containing a majority of the protected acid groups.

5. The photoresist of Claim 1 wherein the photoacid generator is covalently bonded to the branched polymer.

6. The photoresist of Claim 5 wherein the photoacid generator is covalently bonded to the branch segment(s).

7. The photoresist of Claim 6 wherein one of the segments contains greater than 50% of the protected acid groups present in the branched polymer.

8. The photoresist of Claim 7 wherein the branch segment(s) contain greater than 50% of the protected acid groups present in the branched polymer.

9. The photoresist of Claim 1 wherein the branched polymer is comprised of an acrylate polymer, a methacrylate polymer, an acrylate/methacrylate copolymer, and combinations thereof.

10. The photoresist of Claim 1 further comprising a solvent.

11. The photoresist of Claim 1 wherein the branched polymer is formed by addition polymerization of at least one ethylenically unsaturated macromer component and at least one ethylenically unsaturated comonomer.

12. The photoresist of Claim 1 wherein the branched polymer segment is attached to a preformed linear backbone by chemical reaction.

13. The photoresist of Claim 11 wherein

(a) the ethylencially unsaturated macromoner component has a number aveage molecular weight (M_n) in the range of 1000 to 15,000;

(b) the linear backbone segment has a number average molecular weight (M_n) between 2,000 and 500,000; and

(c) the weight ratio of the linear backbone segment to the branch segment(s) is within a range of 50/1 to 1/10.

14. The photoresist of Claim 1 wherein the branched polymer has a glass transition temperature of at least 22°C.

15. The photoresist of Claim 1 further comprising a dissolution inhibitor.

16. The photoresist of Claim 1 wherein the branched polymer is an acrylic/methacrylic/styrenic copolymer being at least 60% by weight acrylate and having at least 60% of methacrylate repeat units present either in a first location or a second location, the first location being one of the segments, the second location being a segment different from the first location, wherein at least 60% of the acrylate repeat units are present in the second location.

17. The photoresist of Claim 1 wherein the branched polymer is a fluorine-containing copolymer comprising a repcat unit derived form at least one ethylenically unsaturated compound containing at least one fluorine atom covalently attached to an ethylenically unsaturated carbon atom.

18. The photoresist of Claim 17 wherein the fluorine-containing copolymer is further comprised of a repeat unit derived from at least one unsaturated compound selected from the group consisting of:

23. The photoresist of Claim 21 wherein the photoacid generator is covalently bonded to the branched polymer.

24. The photoresist of Claim 23 wherein the photoacid generator is covalently bonded to the branch segment(s).

25. The photoresist of Claim 24 wherein one of the segments contains greater than 50% of the protected acid groups present in the branched polymer.

26. The photoresist of Claim 25 wherein the branch segment(s) contain greater than 50% of the protected acid groups present in the branched polymer.

27. A process for preparing a photoresist image on a substrate comprising, in order:

(W) applying a photoresist composition on a substrate, wherein the photoresist composition comprises:

(a) a branched polymer containing protected acid groups, said polymer comprising one or more branch segment(s) chemically linked along a linear backbone segment, wherein the branched polymer contains sufficient functionality to render the photoresist developable to afford a relief image, upon imagewise exposure to radiation selected from the group consisting of ultraviolet and violet and subsequent heating, and wherein the branch segment(s) contain at least two repeating monomer units and have a number average molecular weight (M_n) of at least 1000;

(b) at least one photoacid generator; and

(c) a solvent;

(X) drying the coated photoresist composition to remove solvent and thereby to form a photoresist layer on the substrate;

(Y) imagewise exposing the photoresist layer to form imaged and non-imaged areas; and

(Z) developing the exposed photoresist layer having images and non-imaged areas to form the relief image on the substrate.

28. The process of Claim 27 further comprising a step of heating the photoresist layer following step (X) and prior to step (Z).

29. The process of Claim 27 wherein the photoresist layer is developed with an aqueous alkaline developer.